

# Colloidal ionic complexes on periodic substrates: ground state configurations and pattern switching

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We theoretically and numerically studied ordering of “colloidal ionic clusters” on periodic substrate potentials as those generated by optical trapping. Each cluster consists of three charged spherical colloids: two negatively and one positively charged. The substrate is a square or rectangular array of traps, each confining one such cluster. By varying the lattice constant from large to small, the observed clusters are first rod-like and form ferro- and antiferro-like phases, then they bend into a banana-like shape and finally condense into a percolated structure. Remarkably, in a broad parameter range between single-cluster and percolated structures, we have found stable super-complexes composed of six colloids forming grape-like or rocket-like structures. We investigated the possibility of macroscopic pattern switching by applying external electrical fields.

## I. INTRODUCTION

It is generally considered that the study of colloidal systems started with the work of Thomas Graham, around 1860, although substances such as the “purple of Cassius”, which turns out to be colloidal gold, were used by glass-makers and porcelain manufacturers as early as the XVIIth century [1]. For a long period, those systems were considered as “unmanageable” (see e.g. the preface of Ref. [1]), due in particular to the difficulty to characterize them precisely (size, shape, charge etc) and also to the lack of theoretical tools to understand effective interactions. From this perspective, a decisive step forward occurred in the 1940s with the work of Derjaguin, Landau, Verwey and Overbeek [2], which helped turn the initial empiricism into a more solid body of knowledge. More recently, progress in experimental manipulation techniques promoted colloids as interesting model systems to investigate a large gamut of fundamental physical phenomena: phase ordering, nucleation, effects of confinement and reduced dimensionality, interfacial phenomena, and various non-equilibrium problems including glass formation, to name but a few. Indeed, compared to atomic systems, colloids offer four advantages : first, they are characterized by small elastic constants and therefore they are easy to manipulate (“soft matter”); second, they are more easily visualized since their typical length scale is within the range of visible light; third, the corresponding time scale is no longer in the pico-second range, but of order 1s; fourth, their effective interaction potential may be easily tuned to some extent by changing some control parameter such as the concentration of a given solute [3]. Such features stem, directly or indirectly, from the large size (on an atomic scale) of the mesoscopic constituents. Hence, colloids can be considered as “big atoms” [4], but with controllable interactions, and it is noteworthy that they may furthermore exhibit new structures, that do not seem to have any atomic analogue [5].

Of particular interest here is a class of charged colloidal spheres in the presence of optical trap arrays, where a wide variety of crystalline states has been reported [6–12]. On a two-dimensional modulated substrate, multiple charged colloids can be confined in sufficiently strong traps, and thereby form  $n$ -mers which exhibit an orientational degree of freedom. It has been established from experimental, numerical and theoretical approaches [6–12] that such systems may show remarkably rich orientational ordering, and lead to the formation of so called colloidal molecular crystals.

Previous approaches considered situations where the colloids forming trapped  $n$ -mers are like-charged objects. On the other hand, the ‘molecules’ under study here are made up of oppositely charged colloids, with equal charges in absolute value. The focus will be on a square lattice of traps, including also distorted geometries where all distances along one of the principal axis of the square is scaled by a given factor  $\alpha$ , thereby producing a rectangular lattice. We will restrict our attention to the ground state, leaving thermal effects for further studies [13]. Under these circumstances, it has been shown that in the dipolar case (with trapped clusters each formed of two oppositely charged colloids) the resulting orientational behaviour is somehow trivial: the observed phase is made up of ABAB-type stripes, where the dipoles in stripe A are aligned along the stripe (up), while those in stripe B have opposite

orientation [12]. Furthermore, the stripe structure cannot be tuned by modifying the lattice constant or salt content in the solution. Here we consequently consider clusters with three colloids, two negatively and one positively charged, which are more amenable to an external control, and display a wealth of ordering patterns, which is the center of our interest. The paper is organized as follows. The model and the methods are defined in section II, where the differences in modelling with previous works are outlined. Behaviour on square and rectangular lattices with isotropic parabolic confinement potential is studied in section III and in section IV, we discuss the relevance of these results in the case of a more realistic cosine trap potential. All these results pertain to equilibrium configurations, while orientational pattern modifications induced by an external electric field is finally addressed in section V. In the conclusion, we summarize our main findings and discuss perspectives and open problems left.

## II. MODEL AND METHODS

We consider a mixture of negatively and positively spherical and homogeneously charged colloids, with stoichiometry 2:1 (twice more negative than positive macroions, which is equivalent to the situation where all charges are reversed). Those mesoscopic objects bear a total charge that is neutralized by an ensemble of micro-ions. We assume that counter-ions and electrolyte micro-ions do not differ. The colloids are confined in a two dimensional plane by the action of laser beams. This plane is furthermore corrugated by additional preferential confinement: the colloids, subject to gradient forces and light pressure [6, 14] tend to gather in the regions of highest laser intensity. It is then experimentally possible to create a 2D periodic substrate of traps, with variable geometry. It should be emphasized that the micro-ions are not sensitive to confinement, so that our two dimensional colloidal system is immersed in a standard electrolyte, that mediates between the charged colloids a screened Coulomb interaction of the form [2, 15, 16]

$$V_C = K \sum_{j \neq i} s_{ij} \frac{e^{-\kappa r_{ij}}}{r_{ij}/l}. \quad (1)$$

The energy scale  $K$ , which contains a geometric prefactor together with the squared effective charge of the colloids [17], is not relevant for our purposes, since we are interested in ground state configurations. In Eq. (1), the sum runs over all colloidal pairs with interaction sign  $s_{ij} = \pm 1$  distinguishing like- from oppositely charged colloids, and inter-particle distance  $r_{ij}$  between macroions  $i$  and  $j$ ; with  $l$  we denote the intertrap distance, see Fig. 1. We therefore implicitly assumed that oppositely charged colloids at contact also interact through a screened Coulomb form, whereas such a functional dependence is better suited to describe the far-field behaviour [18]. We note however that as long as we are comparing phases with an equal number of doublet +/- at contact, such configurations contribute a constant to the total energy, so that considering more exact forms of interaction potential at short scale would not alter our conclusions. In Eq. (1),  $1/\kappa$  denotes the Debye length, that can be tuned changing the electrolyte density. Strictly speaking, Eq. (1) is not an energy but a free energy, since it includes an entropic contribution from the micro-ions [19].

In addition to inter-particle forces (two-body, and pairwise additive), the colloids feel an external (one-body) potential due to laser modulation, and it is the subtle interplay between both kinds of forces that selects the type of ionic complexes that is formed in each trap, and their relative arrangement from trap to trap. In [8, 9], it was assumed that the colloidal complexes in a given trap (dimers, trimers etc) form a rigid object, with a single orientational degree of freedom, which effectively allows to omit the laser-induced potential in the analysis. The situation with oppositely charged colloids however differs: take an isolated triplet -/+/-, in the aligned geometry which minimizes its self energy. Such an object invariably bends under strong confinement thereby forming a ‘banana-like’ object. The shape of the banana depends on the parameters (salinity, inter-trap distance etc), and should be determined self-consistently. We therefore do not lump substrate potential effects into a unique quantity as in [8, 9], but explicitly consider each colloidal degree of freedom in the analysis. This rules out the discrete angle approach invoked in [9], where only a restricted set of possible orientations were considered. We also note that already at the level of like-charged colloids, our recent work [10] evidenced some subtle shortcomings of the rigid  $n$ -mer approach.

The system obviously bears some resemblance to the molecules on the atomic scale. However, in our model the binding is the result of the attractive Yukawa interactions and the confinement potentials and is therefore relatively weak compared to the strong covalent bonds typical in real molecules. We have consequently chosen to call the  $n$ -meric colloidal structures “clusters” or “complexes” rather than “molecules” as has been done elsewhere (see [7–10]). In spirit, our study then belongs to a more general line of research pertaining to colloidal clusters [20]. The previous references though generally deal with large assemblies, whereas our clusters are made up of a small number of colloids.

In all our considerations, the ratio of the total number of colloids to the total number of traps is exactly three, therefore under strong enough confinement, there are exactly 3 colloids per trap and the ground state is paved with trimers ( $- + -$ ) of varying shapes and orientations. These mesoscopic objects bear a net charge, which is neutralized

by micro-ions in solution. It has been realized [8, 10] that it is not necessary to invoke local anisotropies of the confinement potential to account for the observed ground states: there is an obvious source of anisotropy in the lattice geometry itself; however, in the vicinity of a trap minimum, the confined particles feel an isotropic (2D) potential. In this case, the screened Coulomb potential alone is able to select preferred orientations for the clusters (whereas as alluded to above, the effective spin model considered in [9] restricted possible orientations to the principal directions of the light lattice). Here we wish to avoid introducing an orientational bias through the trap potential, and therefore initially consider the parabolic confinement. The total dimensionless energy of colloid  $i$  reads

$$e_i = A(\delta_i/l)^2 + \sum_{j \neq i} s_{ij} \frac{e^{-\kappa r_{ij}}}{r_{ij}/l}, \quad (2)$$

where  $\delta_i$  denotes the distance between colloid  $i$  center of mass and the center of the trap to which it belongs, and  $A$  measures the relative importance of parabolic confinement over Coulombic forces. Each triplet of colloids belongs to a ‘native’ trap, so the colloids are not allowed to hop from one trap to another. Such a limitation precludes the sliding states studied in [21] under the influence of an external electric field. We note that the experimental situation is somehow intermediate between the point of view adopted here – *a priori* mostly relevant for strong confinement conditions –, and that used in [9], see the discussion in [10]. For completeness, we have also performed simulations with a ‘realistic’ potential in the spirit of [7] to assess the validity of the isotropic approach.

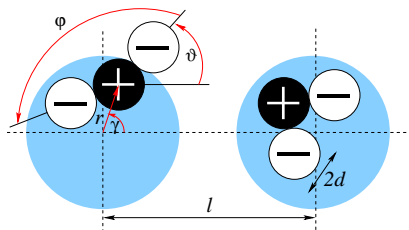


FIG. 1: (Color online) Sketch of two clusters – each made up of three colloids – in two different potential traps, with definition of the relevant quantities. The center of a blue area denotes the confining potential minimum and  $l$  is therefore the intertrap distance. In all the paper, the same color code will be used: black (resp. white) dots for positively (resp. negatively) charged colloids.

At constant temperature, three parameters govern the behaviour of the system: the relative magnitude of the confinement with respect to the Yukawa interaction  $A$ , the ratio of the colloid radius to the Debye screening length  $\kappa d$ , and the ratio of the lattice spacing to Debye length  $\kappa l$ . In the rectangular case, the lattice aspect ratio  $\alpha$  should be included. A trimer in two dimensions has six degrees of freedom, but only four of them are independent assuming the colloids are in contact. The arrangement of colloids in the vicinity of a trap center can therefore be described by four quantities (see Fig. 1): the position of the cluster's center of mass relative to the trap minimum is described by  $r$  and  $\gamma$ , the relative orientation of its axis with respect to a fixed direction (say a line joining the centers of two neighboring traps) by the angle  $\vartheta$  and the amount of bending by  $\phi$  ( $\phi = \pi$  for rod-like and  $\phi < \pi$  for bent structures).

Ground state configurations were obtained by energy minimization (EM) technique and tested by standard Monte Carlo (MC) annealing simulations. In order to reduce the number of minimizing parameters in EM, an assumption on the ground state structure was preset. For a given rectangular lattice we decided to partition the lattice to 2 (A-B) or 4 (A-B-C-D) sub-lattices, which in general form a checkerboard or a stripe (chain) pattern. Since each colloidal cluster is parametrized by four quantities (see Fig. 1), a  $p$ -partite ( $p = 2, 4$ ) assumption in EM would correspond to  $4p$  minimizing parameters. We used standard numerical routines (simplex and quasi-Newton algorithm [22]) for finding the (local) minimum; by repeating the EM procedure several ( $\sim 10^4$ ) times over  $4p$  different initial estimates, we eventually converged to a global minimum. However, in extreme parameter regimes (i.e.,  $l/d \gg 1$  or close to phase transitions), the convergence became slower due to many almost degenerate local minima and the ground state was identified among selected candidates - by directly comparing their energies.

The 2- and 4-partite constraint used in EM was further assessed by standard MC annealing simulations. We checked all interesting regions of the phase diagram by running several MC simulations starting from different initial configurations (both minimal or close-to-minimal EM structures and random configurations) and used the annealing method with exponentially decaying temperature profile. We tried several system sizes with  $2 \times 2$ ,  $4 \times 4$  and  $16 \times 16$  number of traps using periodic boundary conditions. As a result, we identified and confirmed all shapes obtained in EM. However, due to the tiny energy differences and large energy barriers between local minima, long relaxation times (i.e.,  $10^8$  MC steps for  $4 \times 4$  system array) were needed to obtain exactly the same orientational orders as in EM. Hence, the system easily gets trapped at low annealing temperature in some local metastable phase composed of domains of various ground state patterns [23].

### III. SQUARE AND RECTANGULAR LATTICE CONFINEMENT

Before embarking on a detailed study, we first give an overview (Fig. 2) of the various composite objects that we have observed in our simulations. When the traps were well separated, we observed isolated trimers, either straight or banana-shaped  $\mathcal{B}$ . For very small trap separation  $l$ , percolated chain-like structures  $\mathcal{C}$  rather than clusters are stable. In the intermediate region “super-clusters” composed of six colloids appear. They are formed by two neighbouring trimers forming the super-cluster by minimizing their total energy (paying the penalty due to the confinement while reducing the electrostatic interaction energy) [24]. We observed two typical shapes and coined them grape  $\mathcal{G}$  and rocket  $\mathcal{R}$ . In Fig. 3 we further provide a summary of different orientational orderings and propose a nomenclature to classify them.

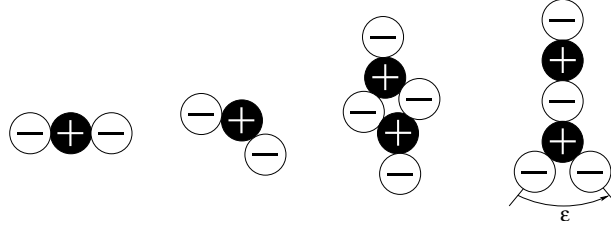


FIG. 2: Summary of the most frequent composite clusters encountered in our study (from left to right): straight trimer, banana  $\mathcal{B}$ , grape  $\mathcal{G}$ , rocket  $\mathcal{R}$ .

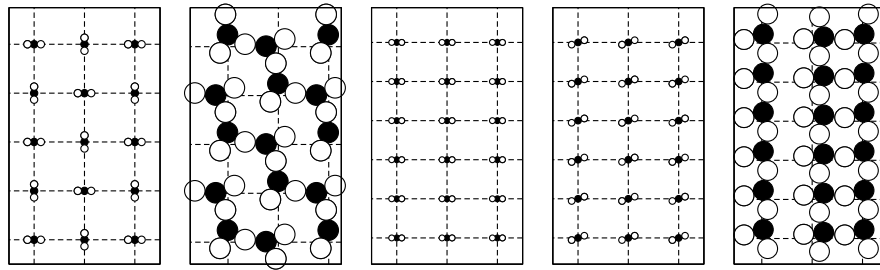


FIG. 3: Sketch of the different ordering patterns that will be reported (from left to right): anti-ferro  $\mathcal{A}$ , chain  $\mathcal{C}$ , ferro  $\mathcal{F}$ , tilted ferro  $\mathcal{F}^*$  and ladder  $\mathcal{L}$ . Dashed lines represent a square (or rectangular) lattice of traps.

#### A. Square lattices

Figures 4 and 5 show the type of orderings which occur on a square lattice ( $\alpha = 1$ ), at two different pinning amplitudes (embodied in the parameter  $A$ ). On panel a) we show the phase diagram separating the regions of stability of phases and the corresponding snapshots of the typical cluster arrangements. The panels b) and c) display the variation of three quantities characterizing the cluster shape and their orientational ordering. The transitions from straight to bent shapes are clearly seen on bifurcating red curves. It should be stressed that  $\phi$  and  $2\pi - \phi$  represent the same shape and the two branches do not indicate two different structures. The black curves showing the cluster orientation have two branches with  $\vartheta_1$  and  $\vartheta_2$ . The special case is the  $\mathcal{A}$  (antiferro) phase, where  $(\vartheta_1, \vartheta_2) = (0, \pi/2)$ . For straight clusters the angles  $\vartheta$  and  $2\pi - \vartheta$  are equivalent, but this is no longer true if they are bent. Therefore, the region with four distinct branches on Fig. 5 represents a 4-partite structure with  $\vartheta_1 \dots \vartheta_4$ . The values of  $r$  (green curves) tell us whether the clusters are displaced from the trap minima ( $r \neq 0$ ) or not ( $r = 0$ ). The values of the fourth defining quantity  $\gamma$  proved rather uninformative and were not included in the figures for clarity reasons.

At the stronger confinement (Fig. 4) we found three phases: isolated triplets in the anti-ferro like arrangement  $\mathcal{A}$ , bent (banana) triplets  $\mathcal{B}$  whose angular arrangement varies continuously to anti-ferro  $\mathcal{A}$  upon increasing  $l/d$ , and a percolated chain pattern ( $\mathcal{C}$ ) at very low  $l/d$  and small screening (lower left corner of Fig. 4a)). At weaker confinement (Fig. 5), two additional phases appear: rocket  $\mathcal{R}$  and grape  $\mathcal{G}$ , which are both non-percolating, and made up of the repetition of 2-triplet (6 colloids) objects.

In Fig. 4, all ground state configurations have a 2-partite lattice structure, which has also been confirmed by the unconstrained MC annealing simulations. In the limit of small macro-ions,  $l/d \gg 1$ , we find stable isolated triplet

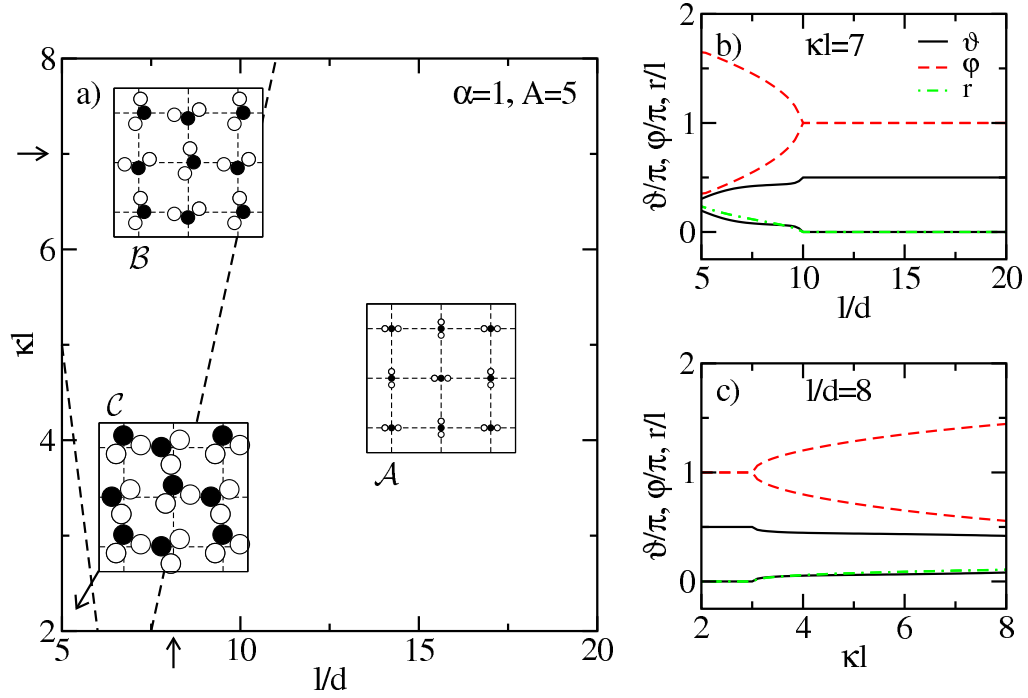


FIG. 4: (Color online) **a)** Ground state phase diagram at a relatively strong substrate potential ( $A = 5$ ) for colloidal trimers on a square lattice. Typical snapshot configurations are calculated using  $(l/d, \kappa l) = (7, 2)$  for the  $\mathcal{B}$  phase,  $(15, 4)$  for the  $\mathcal{A}$  structure, and  $(5, 2)$  for the  $\mathcal{C}$  phase. The lines between the different phases are shown as a guide to the eye. **b)** Values of the three quantities characterizing the cluster shape: (red dashed (upper):  $r$ , black solid:  $\vartheta$  and green dot-dashed (lower):  $\varphi$ ), as a function of the ratio  $l/d$  at constant  $\kappa l = 7$ . **c)** Values of the same three quantities as a function of  $\kappa l$  at constant  $l/d = 8$ .

configurations with quasi degenerate orientational preferences. For example, the anti-ferro  $\mathcal{A}$  phase is slightly more favorable compared to the tilted ferro  $\mathcal{F}^*$  phase: at the  $(l/d, \kappa l) = (15, 4)$  point in the phase diagram the corresponding energies are  $E_{\mathcal{A}}/K = -2.4250$  and  $E_{\mathcal{F}^*}/K = -2.4247$ .

In Fig. 5 there are regions in the phase diagram where the 4-partite configurations appear to be favored over bipartite. The energy difference between 2- and 4-partite ordering, however, is extremely small. For example, in the representative rocket  $\mathcal{R}$  and grape  $\mathcal{G}$  phases shown in Fig. 5(a) the energies are respectively  $E_{4p}/K = -0.5888$ ,  $E_{2p}/K = -0.5870$  and  $E_{4p}/K = -2.723145$ ,  $E_{2p}/K = -2.723143$ . Such small differences,  $E_{4p} - E_{2p}$ , imply that these ground state configurations become unstable at small but finite temperatures and the formation of domains is expected in experiments and simulations. Similar effect is expected also for the  $\mathcal{A}$  ground state, which should interfere with nearest (in energy)  $\mathcal{F}^*$  phase, as in the previous  $A = 5$  case in Fig. 5. On the other hand, the grape  $\mathcal{G}$  phase in the  $l/d \gg 1$  limit is well separated from the competing  $\mathcal{A}$  phase ( $E_{\mathcal{A}}/K = -2.645310$  for the same  $\kappa l$  and  $\kappa d$  values).

### 1. Antiferro-like phase

The occurrence of the  $\mathcal{A}$  phase on the right hand-side of Figs. 4 and 5 can be rationalized following similar lines as in Ref. [8]. For large enough values of  $\kappa l$  and even larger  $l/d$ , it is legitimate to restrict the summation in Eq. (2) to nearest neighbor traps (see [10] for a more complete discussion). It is also legitimate to assume that triplets align in straight configurations. The question is therefore to understand the relative orientation of triplets, from trap to trap. Elaborating on the remark, put forward in [25, 26], that a non isotropic charge distribution in an electrolyte, creates an electric potential that is anisotropic at all scales and that does not have any simple ‘multipolar’ symmetry, we write the angular dependence of the far field potential of a triplet as [8]

$$V_{tr} = 2 \cosh(2\kappa d \sin \psi) - 1 \quad (3)$$

where the direction  $\psi$  is defined in Fig. 6-a). Consequently, the relevant angular dependent triplet-triplet interaction potential may be written (see Fig. 6-b)):

$$V_{tr/tr} = [2 \cosh(2\kappa d \sin \psi_1) - 1] [2 \cosh(2\kappa d \sin \psi_2) - 1]. \quad (4)$$

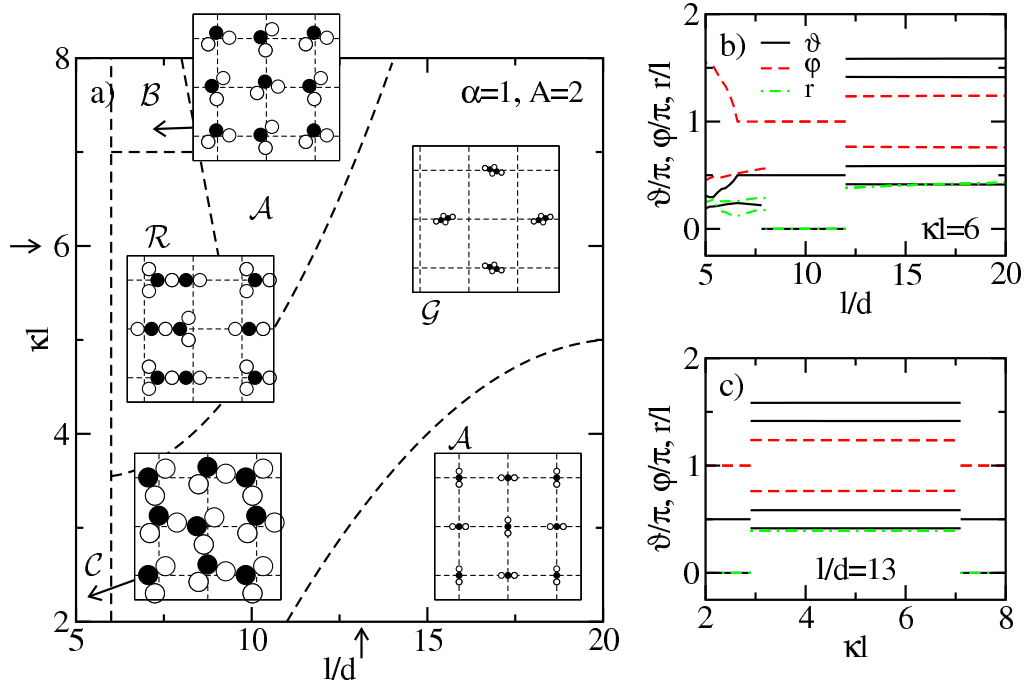


FIG. 5: (Color online) Same as Fig. 4 but for a relatively weak substrate potential ( $A = 2$ ). **a)** Typical snapshot configurations are calculated using  $(l/d, \kappa l) = (7, 8)$  for  $\mathcal{B}$ ,  $(7, 4)$  for  $\mathcal{R}$ ,  $(5, 2)$  for  $\mathcal{C}$ ,  $(20, 8)$  for  $\mathcal{G}$ , and  $(15, 2)$  for  $\mathcal{A}$  phase.

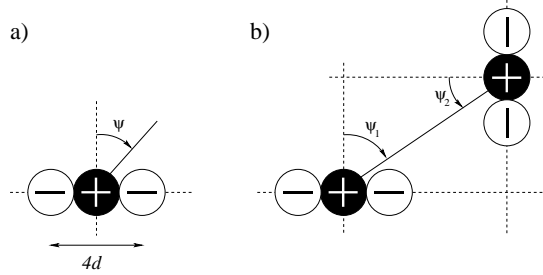


FIG. 6: Definition of the notations used to compute triplet-triplet interaction in the (aligned) straight case.

On a square lattice, and assuming bipartite structure (which is backed up by simulations), we then have to consider triplet-triplet interactions along both principal axis of the lattice. This leads to the following energy

$$[2 \cosh(2\kappa d \sin \psi_1) - 1] [2 \cosh(2\kappa d \sin \psi_2) - 1] + [2 \cosh(2\kappa d \cos \psi_1) - 1] [2 \cosh(2\kappa d \cos \psi_2) - 1]. \quad (5)$$

The minimum is reached for  $(\psi_1, \psi_2) = (0, \pi/2)$ , irrespective of  $\kappa d$ , which exactly coincides with the  $\mathcal{A}$  phase configuration. The situation changes on a rectangular lattice, see below. On the other hand, the  $\mathcal{A} \rightarrow \mathcal{B}$  transition line observed in Fig. 4 can be explained as a one-cluster effect: in the absence of confinement, the trimers take on the straight shape due to the repulsion between the two positively charged colloids. However, by increasing the confinement or because of enhanced screening, the relative importance of the electrostatic repulsion decreases. We expect that for  $A$  and  $d$  fixed, there exists a critical inverse screening length  $\kappa^*$  beyond which the straight trimer bends (and ultimately forms an equilateral triangle if  $\kappa$  is very large). Since it is a one-triplet instability,  $\kappa^*$  should be independent of lattice spacing  $l$  which translates into a straight line with slope  $\kappa^* d$  in a  $(\kappa l, l/d)$  plot such as Fig. 4(a). This corroborates our numerical finding with a straight separatrix between  $\mathcal{A}$  and  $\mathcal{B}$  phases. For  $A = 2$ , the argument does not hold since no transition from straight to bent shapes takes place.

## 2. Grape phase

The stability of the grape phase  $\mathcal{G}$  can be rationalized by comparing the self-energy per colloid

$$E_{self} = \frac{d}{6} \sum_{j \neq i=1}^6 s_{ij} \frac{e^{-\kappa r_{ij}}}{r_{ij}} \quad (6)$$

of different composite complexes in the absence of any trap potential. In Fig. 7 we have compared the self-energies of

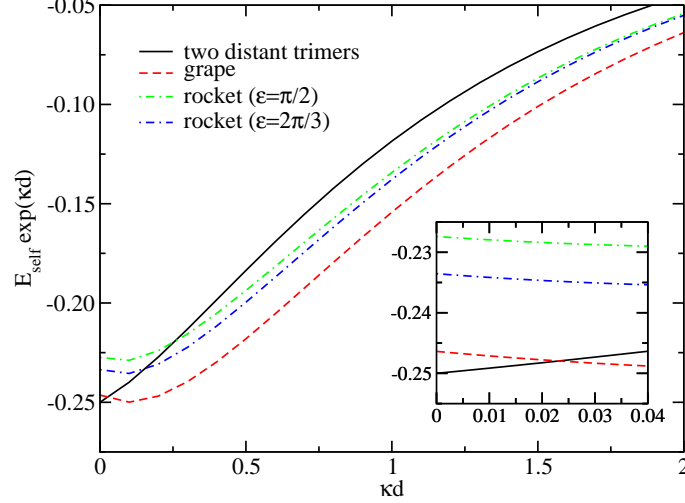


FIG. 7: (Color online) Coulombic self-energy of 6 colloids (2 positively, and 4 negatively charged) forming various complexes.

the following six-colloid objects: grape, rocket (with various angles  $\epsilon$ , as defined on Fig. 2) and two distant trimers. Among these, the two distant trimers are the most stable in the bare Coulomb limit ( $\kappa \rightarrow 0$ ) with  $E_{self} \rightarrow -1/4$ . However, as soon as  $\kappa d > 2.2 \cdot 10^{-2}$ , a fairly small number, the grape geometry is found to be the optimal one. Therefore, in almost the entire range of relevant values, the grape is energetically the most stable isolated object consisting of six colloids. Of course, on a corrugated substrate, the confining potential influences the above scenario by penalizing extended structures, and the inter-cluster interaction affect the picture as well, however, there is still a substantial region on Fig. 5 and 8 (see below) where the grape phase remains stable.

## B. Rectangular lattice of traps

Distorting lattice geometry by changing the aspect ratio away from the square shape ( $\alpha \equiv l_y/l_x < 1$ ) induces new orderings to the list of ground state configurations reported above. Figure 8 shows ground state phase diagrams for  $\alpha = 0.8$  and two pinning potentials, where three new phases emerge with respect to the square ( $\alpha = 1$ ) case: a ferro  $\mathcal{F}$  phase and a tilted ferro  $\mathcal{F}^*$  phase, which evolves into a familiar banana  $\mathcal{B}$  phase at smaller  $l/d$  and  $A = 5$ , and a percolating ladder  $\mathcal{L}$  phase in a weaker confinement ( $A = 2$ ). The latter one consists of complex subunits where each trimer touches with three (out of four) neighboring trimers. Both pinning regimes involve also a distorted (or bent) rocket  $\mathcal{R}$  phases, which we identify as a variant of the existing ( $\alpha = 1$ ) phase rather than a new phase itself, and a grape  $\mathcal{G}$  phase with 2- and 4-partite structures. Actually, in Fig. 8(b), almost the whole parameter space is minimized by a 4-partite grape  $\mathcal{G}$  configuration [27].

On a rectangular lattice, we can follow a similar line of reasoning as above in section III A, where the occurrence of the  $\mathcal{A}$  phase was justified. In contrast to the situation on the square lattice, on the rectangular lattice the number of nearest neighbor traps decreases to two and in order to assess the stability of the  $\mathcal{F}$  phase, it is sufficient to consider a single triplet-triplet interaction of the form Eq. (4). In this case, the lowest energy configuration corresponds to parallel triplets ( $\psi_1 = \psi_2 = 0$ ) forming a ferromagnetic-like arrangement along the longest direction of the lattice unit cell. This is indeed what is observed in Fig. 8(a) (see the  $\mathcal{F}$  region on the right hand side), but not in Fig. 8(b), because in this latter case, confinement strength is too weak to prevent neighboring traps from sharing their macroions. We further note that the  $\mathcal{F}^* \rightarrow \mathcal{B}$  transition visible in Fig. 8(a) falls in the same category as the  $\mathcal{A} \rightarrow \mathcal{B}$  seen in Fig. 4: it is a one-cluster instability due to the competition between Coulomb and confinement forces. It is

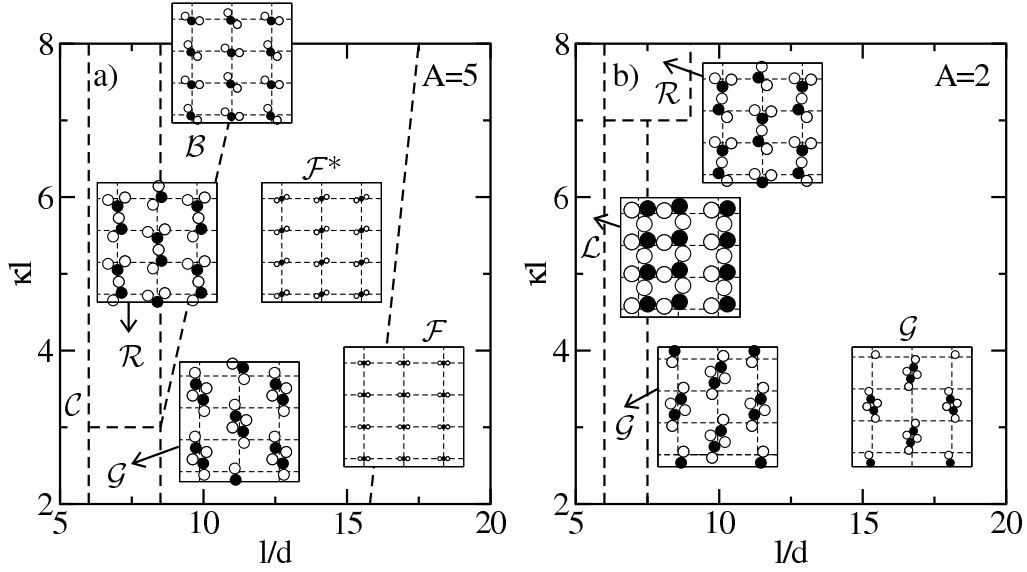


FIG. 8: Ground state phase diagram for colloidal trimers on a rectangular lattice with  $\alpha = 0.8$  and **a)**  $A = 5$  or **b)**  $A = 2$ . Typical snapshot configurations in **a)** are calculated using  $(l/d, \kappa l) = (10, 8)$  for  $\mathcal{B}$ ,  $(7, 4)$  for  $\mathcal{R}$ ,  $(7, 2)$  for  $\mathcal{G}$ ,  $(15, 6)$  for  $\mathcal{F}^*$ , and  $(20, 2)$  for  $\mathcal{F}$  phase; in **b)**  $(l/d, \kappa l) = (7, 8)$  for  $\mathcal{R}$ ,  $(5, 6)$  for  $\mathcal{L}$ ,  $(7, 2)$  for 2-partite  $\mathcal{G}$ , and  $(10, 2)$  for 4-partite  $\mathcal{G}$  phase.

hence not surprising to find that the slopes of both separatrices are close: they are quantified by the same critical screening coefficient  $\kappa^*$  introduced above.

#### IV. TOWARDS A MORE REALISTIC TRAP POTENTIAL

On a realistic trap, when allowing the particles to hop, we can expect to significantly extend the stability of the grapes, at least as soon as  $\kappa d$  exceeds a small threshold. This is supported by the evaluation of the self energies on Fig. 7 and we further analyzed the stability of the grape phase by explicitly introducing a cosine potential, which provides a reasonable approximation for a realistic optical confinement [7]:

$$V_T^{real} = -\frac{A_r}{2\pi^2} (\cos(2\pi x/l) + \cos(2\pi y/\alpha l)). \quad (7)$$

The prefactor  $2\pi^2$  is chosen such that both realistic and simplified potentials behave in the same way, as  $(\delta/l)^2 = (x^2 + y^2)/l^2$  close to the trap minimum, when one chooses  $A = A_r$ .

In Figs. 9(b,c,d) we show ground state configurations for various pinning strengths  $A_r$  using the same parameter values  $(l/d, \kappa l, \alpha)$  as in Fig. 9(a) where we show the four most representative parabolic-trap configurations. We choose  $A_r$  such that both potentials become similar in amplitude at the point of maximum  $V_T^{real}$  (see left panel of Fig. 9). As  $A_r$  gets smaller (going from Fig. 9(b) to Fig. 9(d)), the optimal configurations indeed evolve to the grape  $\mathcal{G}$  geometry. In the limit  $A_r \rightarrow A$ , i.e., when the potentials share the same behaviour close to the trap center, the lowest configurations are always grape  $\mathcal{G}$  phases. Although having the same internal structure, these grapes are formed in realistic trap minima rather than at trap midpoints. In addition, the orientation of grapes is selected by the symmetry of the underlying realistic potential  $V_T^{real}$ , which is lowered with respect to the isotropic parabolic trap (the inset in the left panel of Fig. 9 shows the equipotential lines of  $V_T^{real}$ ). In fact, the realistic trap square symmetry is manifested in all configurations shown in Figs. 9(b,c,d).

From Fig. 9, we see that switching to realistic trap potential ( $V_T^{real}$ ) preserves some typical cluster shapes (e.g., straight trimer, grape  $\mathcal{G}$ , rocket  $\mathcal{R}$ ) from the parabolic case, while the positional or/and orientational order is generally altered. In a simple picture, the full consistency of both potentials (if any) would be found near the bottom of the trap where the realistic potential becomes isotropic, i.e., for  $l/d \gg 1$ . Since small  $A_r$  favor grape configurations that violate both the positional and orientational orders of the parabolic case, the consistency should be rather searched in the opposite limit of strong  $A_r \gg 1$ , where each trap should host exactly 3 colloids. In particular, the most promising phases are  $\mathcal{F}$  and  $\mathcal{A}$  phases since they also obey the symmetry constraints of  $V_T^{real}$ . To avoid bending of extended trimers in these two phases, we also anticipate small screening, i.e.,  $\kappa d \ll 1$ , otherwise a banana  $\mathcal{B}$  shape might become more favorable.



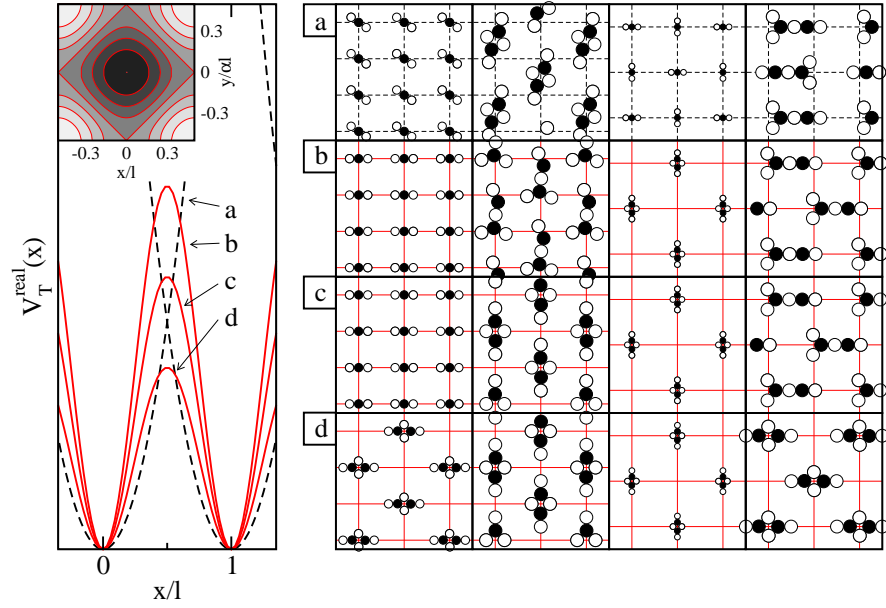


FIG. 9: (Color online) Comparison of structures calculated within an isotropic parabolic potential (a) and realistic cosine potential  $V_T^{\text{real}}$  (b-d) with three neighboring magnitudes  $A_r$  chosen to roughly correspond to the parabolic potential at the trap midpoint  $x/l = 0.5$  (left panel). In (a) the parameter values are, from left to right:  $(l/d, \kappa l, A, \alpha) = (10, 4, 5, 0.8)$  ( $\mathcal{F}^*$  phase),  $(7, 2, 2, 0.8)$  ( $\mathcal{G}$  phase),  $(15, 4, 5, 1)$  ( $\mathcal{A}$  phase), and  $(7, 4, 2, 1)$  ( $\mathcal{R}$  phase). In (b-d) we use the same parameters as in (a) except  $V_T^{\text{real}}$  is used instead of parabolic trapping with  $A_r = 20, 15, 10$  for  $A = 5$  and  $A_r = 8, 6, 4$  for  $A = 2$ .

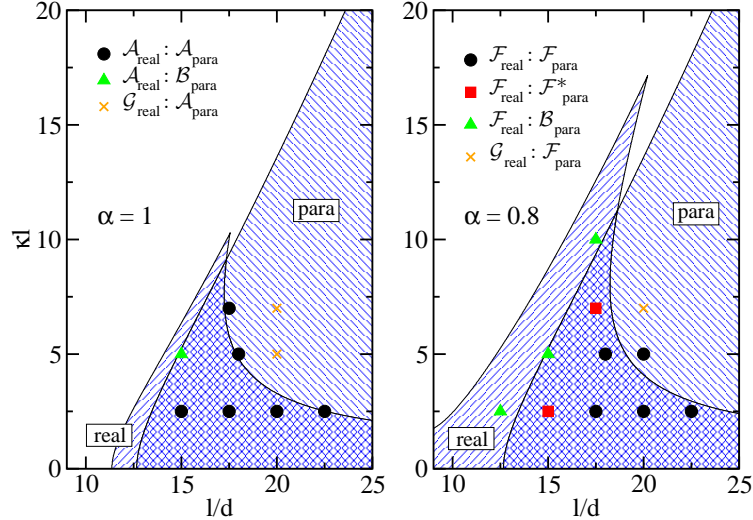


FIG. 10: (Color online) Single-trap calculations for parabolic (para) and realistic (real) trap potentials using  $A = A_r = 50$  and  $\alpha = 1$  (left panel) and  $\alpha = 0.8$  (right panel). Shaded areas denote regions in parameter space where straight-trimer has lower energy than a banana  $\mathcal{B}$  and grape  $\mathcal{G}$  clusters. The symbols are comparing full energy-minimization calculations for both trap potentials considering all neighboring traps: black disks denote exact consistency while the other symbols indicate that different phases are found with the ‘realistic’ and parabolic confinement potentials.

Following these criteria and using a single-trap approximation (which is justified for small clusters), we identified regions in the  $(\kappa l, l/d)$  parameter space (see shaded areas in Fig. 10) where one straight-trimer is energetically favorable against the banana  $\mathcal{B}$  and grape  $\mathcal{G}$  structures. In Fig. 10 we show such regions for realistic and parabolic potentials for a square and rectangular case (note that  $\alpha$  has no effect in the parabolic approximation). The overlap between them gives an estimate where the consistency for  $\mathcal{F}$  (in  $\alpha = 0.8$ ) and  $\mathcal{A}$  (in  $\alpha = 1$ ) should be searched within a proper calculation including all neighboring traps. We have checked this at few points of the phase diagram (symbols in Fig. 10) and indeed found consistency: denoted by black circles in Fig. 10 are the results where the all-neighbour

calculation predicts the same phase ( $\mathcal{F}$  in Fig. 10a and  $\mathcal{A}$  in Fig. 10b) for both potentials. These results agree with the single trap prediction. To the left from the overlapping region (at smaller  $l/d$ ), the inclusion of the neighboring traps introduces bending of the trimers and thus prefers banana  $\mathcal{B}$  phase over the  $\mathcal{F}$  or  $\mathcal{A}$  (see green triangles in Fig. 10). This effect is more visible for parabolic potential since it is stronger than realistic when  $A = A_r$ . The above calculations were performed for a rather strong pinning strength ( $A = A_r = 50$ ); however, we have checked and found  $\mathcal{F}$  and  $\mathcal{A}$  consistency also for weaker trap potentials, with  $A = A_r \gtrsim 10$ .

## V. APPLYING AN EXTERNAL ELECTRIC FIELD

Since most of the observed phases are generally close in energy, it is tempting to explore how an external perturbation could change the phase behaviour. We studied the response of the system to a static uniform electric field  $\mathbf{E}$  with the in-plane direction. Our primary purpose was to numerically investigate the possibility of external pattern switching between the known phases, which might be appealing for experimental realizations. The ability to create and control colloidal crystal structures indeed has a wide range of applications in photonic and phononic materials, optical switches, photonic band-gap materials, and self-assembly of nanostructures [11].

In addition to either parabolic or cosine confinement, we use the following field potential at position  $(x, y)$ :

$$V_E = \pm E_0(x \cos \beta + y \sin \beta)/l, \quad (8)$$

where  $E_0$  is a dimensionless field strength measuring the relative importance of external drag forces over Coulombic forces, and  $\beta$  is an angle between  $\mathbf{E}$  and the longest lattice principal axis. The “ $\pm$ ” sign selects between positively and negatively charged colloids, respectively. The amplitude  $E_0$  is considered small enough so that system acquires equilibrated ground state configuration. This requirement is easily fulfilled in a parabolic trap approximation where, in principle, we never reach stationary regimes with drifting colloids [21] even for largest values of  $E_0$ . However, the opposite may happen in a realistic trap confinement [21] where at critical  $E_0$  either cluster hopping or its breaking into smaller constituents takes place. We note that in the later case the critical field can be expressed analytically by  $E_{c,2} = (1 + 2\kappa d) \exp(-2\kappa d)/(2d/l)^2$  above which the two oppositely charged colloids (a dimer) unbind. The breaking of a trimer occurs at slightly lower fields that can be estimated numerically by  $E_{c,3} \sim 0.8E_{c,2}$ .

We examined the influence of  $\mathbf{E}$  on the selected phases shown in Secs. III and IV using the EM and the gradient descent method. In Fig. 11 we show the results (one-trap snapshots) for parabolic trapping. Apart from rather trivial

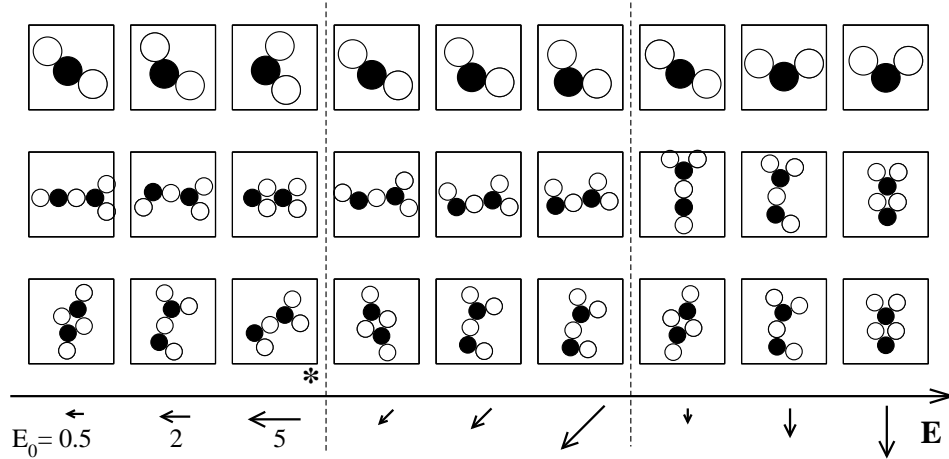


FIG. 11: Application of the external electric field  $\mathbf{E}$  on colloidal clusters shapes in parabolic pinning regime for three field strengths  $E_0$  and directions depicted at the bottom of the figure. The other parameters are:  $(l/d, \kappa l, A, \alpha) = (10, 4, 5, 0.8)$  in first row,  $(7, 4, 2, 1)$  in second row, and  $(7, 2, 2, 0.8)$  in third row. The asterisk symbol indicates that a cluster (when viewed periodically on a lattice) forms a percolated structure along the field direction.

effects, such as bending (formation of the  $\mathcal{B}$  shape out of the straight trimer, or a rocket  $\mathcal{R}$  deformation for  $E_0 \leq 2$ ), we identified also more interesting effects at strongest  $E_0 = 5$ : a new shape evolved from  $\mathcal{R}$  as well as  $\mathcal{G}$  structure, and an elongation of the modified  $\mathcal{G}$  complex along the field direction lead to the formation of the percolated chain structure (denoted by asterisk symbol in Fig. 11).

In a similar manner, we demonstrate in Fig. 12 the influence of  $\mathbf{E}$  on a particular  $\mathcal{A}$  phase, again within a parabolic trap confinement; for  $E_0 = 2$  and an electric field angle  $\beta = 0$  or  $\pi/4$ , we identify a pattern switching to a (quasi)  $\mathcal{F}^*$

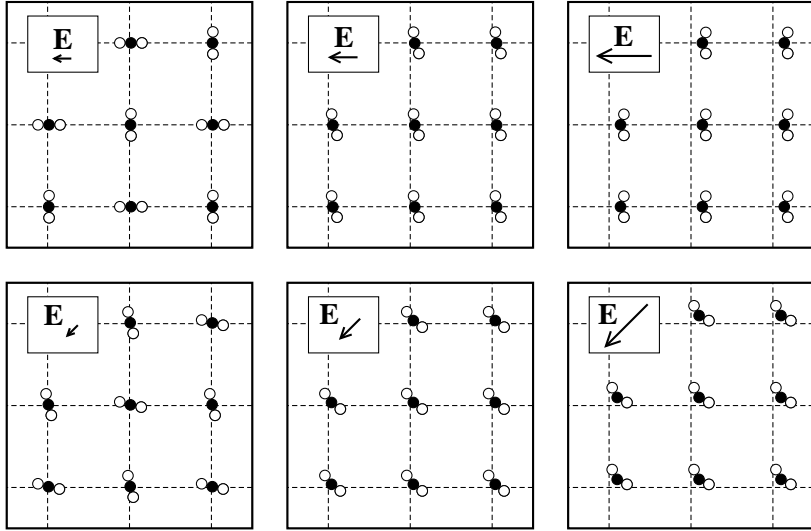


FIG. 12: Influence of an external electric field  $\mathbf{E}$  on the  $\mathcal{A}$  phase within the parabolic trap approximation for  $(l/d, \kappa l, A, \alpha) = (15, 4, 5, 1)$ . The field directions and magnitudes are shown with arrows in the inset of each plot; arrow lengths correspond to magnitudes  $E_0 = 0.5, 2, 5$  of Eq. (8). For  $E_0 = 2$  and  $\beta = 0, \pi/4$  (the middle column) we observe a pattern switching to the  $\mathcal{F}^*$  phase (actually, its close approximation, since the trimers here are slightly bent with  $\varphi_{1,2} \approx 0.91\pi$ ).

phase. Here, the transition  $\mathcal{A} \rightarrow \mathcal{F}^*$  appears to be on orientational basis, with more or less minor shape deformations. Since the trimers of field induced  $\mathcal{F}^*$  phase are slightly shifted away from the trap center, the expected bending due to electric field is (almost) compensated by the restoring trap forces and the clusters appear almost straight.

We have also explored the effect of the external field within the real trap confinement. As found by Reichhardt et al in Ref. [21], the colloids start to flow as soon as the electric field force becomes larger than the real trap confinement, but here we rather focused on static configurations at smaller field strengths. In fact, in a large enough system, any constant electric field would inevitably lead to ground states with uneven population of the traps, i.e. the trimers would prefer to move in the direction of the field to reduce the total energy of the system, leaving some of the traps at the opposite end empty. However, even though such states might have the lowest energy, they might not be accessible in the experiments and simulations. If, for instance, the system is first let to equilibrate at  $\mathbf{E} = 0$  and then a small enough electric field is turned on, a local rather than global minimum is reached with colloids unable to surmount the large energy barriers on the way to the global minimum. This is the regime we are interested in here.

To search for nearest local energy minimum with an increasing electric field, we introduced a gradient descent method (i.e., a method of steepest descent) on a 4-partite lattice (16 model parameters, see Fig. 1) which brings a system continuously from an initial zero-field ground state to a finite-field metastable state using a finite step  $\delta E_0$  (at fixed field direction  $\beta$ ). Depending on the amplitude of the increment  $\delta E_0$ , the switching of the field may be interpreted as fast or slow, something that can also be tuned in an experimental setup and may affect the outcome. In our calculations we tried three step sizes,  $\delta E_0 = 0.01, 0.1, 1$ , and found basically no differences in the resulted configurations.

In Fig. 13 we show the evolution of  $\mathcal{A}$  and  $\mathcal{F}$  phases with increasing  $E_0$  along two field directions using highest field resolution  $\delta E_0 = 0.01$ . Focusing first on the  $\mathcal{A}$  phase (upper row in Fig. 13), we identify at  $E_0 \approx 3$  (for both field directions) a rapid phase transition from a 2- to 1-partite phase, which can be also viewed as a pattern switching to an approximate  $\mathcal{F}^*$  phase (with the internal angle being  $\varphi \approx 0.8\pi$  rather than  $\pi$ ), similar to what we found in the parabolic confinement (middle column in Fig. 12). This tendency of reducing the “partiteness” of the phase by increasing the external uniform field seems natural. However, the opposite situation is observed in the evolution of the  $\mathcal{F}$  phase, shown in Fig. 13(c), where in a short interval,  $3 \lesssim E_0 \lesssim 4$ , the metastable phase adopts a higher, 2-partite  $\mathcal{B}$  structure. This rather surprising effect reflects the richness of the system studied, where the observed phases differ only slightly in energy and can therefore interchange easily under external perturbation. At larger field strengths again a uniform pattern takes place.

We note that a similar field-evolution study in cosine trap confinement was made also for two representative  $\mathcal{G}$  and  $\mathcal{R}$  phases with 6 colloids per trap, but we found no striking effects apart from trivial bending of the clusters, which was already observed in a parabolic confinement (see, e.g., Fig. 11). These results are included in a form of animated cartoons available as online supporting material [29].

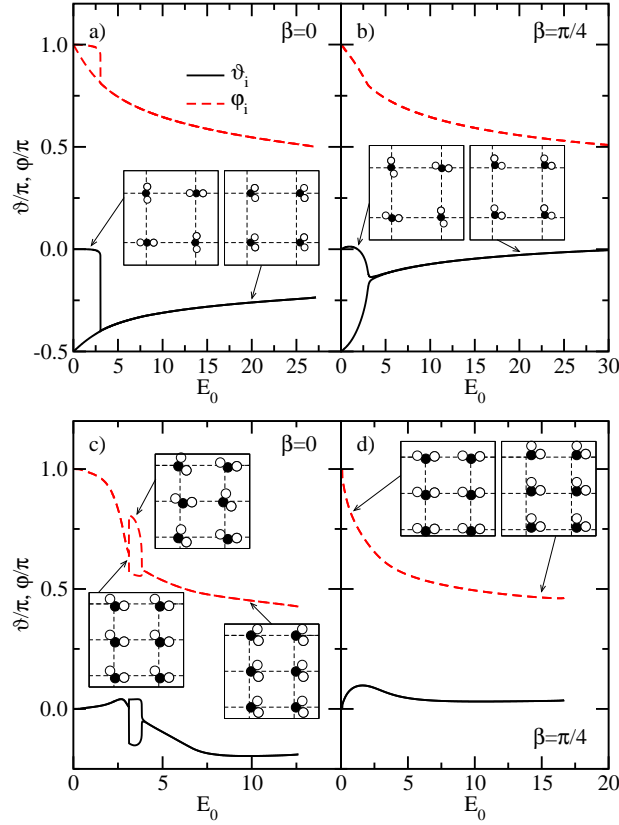


FIG. 13: (Color online) Local energy minima configurations represented by trimer angles  $\vartheta_i$  (solid line) and  $\varphi_i$  (dashed) as a function of external electric field  $E_0$  using the cosine confinement potential Eq. (7). The index  $i = 1...4$  represents the four different values for a 4-partite lattice assumption. The upper row is calculated from initial ( $E_0 = 0$ )  $\mathcal{A}$  phase with  $(l/d, \kappa l, A_r/(2\pi^2), \alpha) = (15, 4, 1.5, 1)$  for two field directions a)  $\beta = 0$  and b)  $\beta = \pi/4$ . In the lower row the initial ( $E_0 = 0$ ) state is the  $\mathcal{F}$  phase with  $(l/d, \kappa l, A_r/(2\pi^2), \alpha) = (10, 4, 0.75, 0.8)$  and field directions are again c)  $\beta = 0$  and d)  $\beta = \pi/4$ . In all the plots we used field resolution  $\delta E_0 = 0.01$ . A few representative snapshots are added for illustration (see the supporting material [29] for the animated cartoons).

## VI. CONCLUSION

In summary, we have studied ordering of colloidal ionic trimers on square lattices. We observed a rich variety of crystal structures including crystals made of complex 6-colloid subunits. We have discussed their stability and the possibility for pattern switching by external control, which might be appealing for experimental realisations and applications.

In case of the isotropic confinement potential, the symmetry is broken by the Yukawa interactions only. The orientational ordering is of ‘intrinsic nature’ and does not stem from an anisotropy present in the confinement potential itself. Three colloids can form a straight line or a bent banana shaped trimer. We have identified the parameter range where both are stable and the types of their orientational ordering. In the low  $\kappa$  and small  $l/d$  part of the phase diagrams, where the inter-cluster interactions typically outweigh the confinement, the neighboring trimers cluster into larger complexes consisting of six colloids; their typical shapes being grape and rocket. At even smaller  $l/d$  and  $\kappa$ , the colloids form percolated structures. Here, however, many-body effects [30] are expected to become significant and our assumption of the pairwise additivity of the colloid-colloid interaction becomes questionable [31, 32]. We have shown that most of the phases observed in the isotropic confinement persist also in the more realistic anisotropic external potential, provided that the confinement strength is large enough. However, their orientational ordering in the latter case is different due to the additional symmetry breaking by the laser field. The rich selection of the ground state structures and the relatively small energy differences between them enable efficient control over the structures by applying external fields. We have analysed the effect of a small external electric field and have shown that it can be used as a pattern switching tool.

Not addressed here, but a subject for future work, is the thermal behaviour of the system. Another question lies in the effect of the interaction potential details on the stability of the observed structures, and in the many-body

interactions among colloids that are expected to be important at high densities. Finally, in addition to systems with oppositely charged colloids, externally driven superparamagnetic colloids [33] and colloids interacting via Casimir interaction in critical binary mixtures [34] may offer instances where the present predictions –or adaptations thereof– could be realized.

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external confinement and the colloidal interactions governs its behaviour.

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